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FORM PTO-1390 (REV. 5-93) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER **10191/1977**
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/913374

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED:
PCT/DE00/00406	**11 February 2000 (11.02.00)**	**12 February 1999 (12.02.99)**

TITLE OF INVENTION
PROTECTIVE LAYER

APPLICANT(S) FOR DO/EO/US
Thomas BRINZ, and Andreas HENSEL

Applicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have. been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☒ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information. International Search Report (translated), Preliminary Examination Report and PCT/RO/101.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s)	:	BRINZ et al.
Serial No.	:	To Be Assigned
Filed	:	Herewith
For	:	PROTECTIVE LAYER
Art Unit	:	To Be Assigned
Examiner	:	To Be Assigned

Assistant Commissioner
for Patents
Washington, D.C. 20231
Box Patent Application

PRELIMINARY AMENDMENT AND
37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT

SIR:

Please amend the above-identified application before examination, as set forth below.

IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

IN THE CLAIMS:

On the first page of the claims, first line, change "What is claimed is:" to: --What Is Claimed Is:--.

Please cancel original claims 1 to 12, without prejudice, in the underlying PCT Application No. PCT/DE00/00406.

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Please add the following new claims:

13. (New) A protective layer that is relatively permeable for CO_2 and is relatively impermeable for SO_2, comprising:

a gas-permeable carrier made of a material that is resistant to sulfuric acid media including SO_2 and SO_3; and

a surface that can be exposed to a gas and is provided with an oxidizing agent having an oxidation potential that is sufficient to oxidize SO_2.

14. (New) The protective layer according to claim 13, wherein:

the oxidizing agent is a nonvolatile oxidizing agent.

15. (New) The protective layer according to claim 13, wherein:

the oxidizing agent includes potassium permanganate.

16. (New) The protective layer according to claim 13, wherein:

the gas-permeable carrier includes aluminum oxide.

17. (New) The protective layer according to claim 13, wherein:

the gas-permeable carrier includes at least one tube having an inside wall provided with the oxidizing agent.

18. (New) The protective layer according to claim 17, wherein:

the gas-permeable carrier includes a block having a plurality of axially parallel cylindrical tubes aligned side by side.

19. (New) The protective layer according to claim 18, wherein:

the cylindrical tubes correspond to round cylinders.

20. (New) The protective layer according to claim 17, wherein:

the gas-permeable carrier includes a block having a plurality of tubes arranged side by side in a radial alignment relative to one of a straight line and a point.

21. (New) The protective layer according to claim 20, wherein:

the tubes have a cross section that tapers toward the one of the straight line and the point.

22. (New) The protective layer according to claim 13, wherein:

the gas-permeable carrier includes at least one grid having intersecting grid rods that are provided with the oxidizing agent.

23. (New) The protective layer according to claim 22, wherein:

the gas-permeable carrier includes a block having a plurality of grids stacked one above the other.

24. (New) A CO_2 sensor, comprising:

a protective layer including:

a gas-permeable carrier made of a material that is resistant to sulfuric acid media including SO_2 and SO_3, and

a surface that can be exposed to a gas and is provided with an oxidizing agent having an oxidation potential that is sufficient to oxidize SO_2, the protective layer separating the CO_2 sensor from a room to be monitored for a CO_2 content.

25. (New) The CO_2 sensor according to claim 24, wherein:

the CO_2 sensor is for a smoke detector.

Remarks

This Preliminary Amendment cancels original claims 1 to 12 without prejudice, in the underlying PCT Application No. PCT/DE00/00406. The Preliminary Amendment also adds

new claims 13-25. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. § 1.121(b)(3)(iii) and § 1.125(b)(2), a Marked Up Version Of The Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) are respectfully requested.

The underlying PCT Application No. PCT/DE00/00406 includes an International Search Report, dated July 14, 2000, and an International Preliminary Examination Report, dated March 28, 2001, copies of which are submitted herewith.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

KENYON & KENYON

By: [signature] (Reg. No. 41,172)

Dated: 8/13/01

By: Richard L. Mayer

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[10191/1977]

PROTECTIVE LAYER

Field Of The Invention

The present invention relates to a protective layer which is relatively permeable for CO_2 and is relatively impermeable for SO_2.

Background Information

Such a protective layer is used, for example, to protect a CO_2-sensitive polymer layer of a smoke detector from damage or contamination due to SO_2. Such a CO_2-sensitive polymer layer is used as a gas sensor in a smoke detector to detect a CO_2 content in a room where the smoke detector is installed. The CO_2-sensitive polymer layer preferably has a membrane composed of a polymer matrix (e.g., polydimethylsiloxane), an auxiliary base (tetraalkylammonium hydroxide) and a pH-sensitive dye (e.g., thymol blue or other derivatives). When this CO_2-sensitive membrane is exposed to CO_2, it leads to reversible reactions, preferably detectable by an optical element, in particular also by electrical or mass-sensitive elements, thus permitting an inference regarding the CO_2 content in the room monitored.

However, when this CO_2-sensitive membrane comes in contact with SO_2, it leads to irreversible reactions in the sensor material and thus to destruction of the CO_2-sensitive feature of the sensor. Since this reaction of the sensor membrane to SO_2 is irreversible, SO_2 reaction products accumulate on the membrane, so that even a low SO_2 concentration will damage the sensor membrane over a period of time and decreases its CO_2 sensitivity, so that a smoke detector equipped with such a CO_2-sensitive membrane sensor will ultimately become useless.

Known protective layers are designed as compressed powder pellets or granules which are

relatively impermeable for SO_2 but relatively permeable for CO_2. Likewise, there are known molecular filters which utilize differences in the molecular structure of the CO_2 molecules and are thus relatively impermeable for SO_2 molecules and relatively permeable for CO_2 molecules. However, one disadvantage when such a protective layer is used to protect a CO_2 sensor is that the CO_2 molecules must first penetrate through this protective layer to reach the CO_2 sensor. Accordingly, the period of time needed for the CO_2 molecules to reach the CO_2 sensor may be greatly prolonged. This increase in time has an especially serious effect when the CO_2 molecules are in movement merely due to their temperature-related kinetic energy (Brownian motion) in the absence of a directional flow, which is usually the case in propagation of smoke in the event of a fire. When such a protective layer is then used in a smoke alarm, the response time of the smoke alarm is increased due to the period of time required for the gas molecules to penetrate through the protective layer; in other words, the period of time until the CO_2 sensor detects an elevated CO_2 concentration is longer.

Summary Of The Invention

The protective layer according to the present invention, however, has the advantage that the CO_2 molecules need only a relatively short period of time to penetrate through the protective layer. When using the protective layer according to the present invention in a smoke alarm, this yields the advantage that the lengthening of the response time of the smoke alarm due to the protective layer is reduced.

The present invention is based on the finding that the oxidation product of SO_2, namely SO_3, is a strongly oxidizing and hygroscopic acid anhydride which reacts further immediately to form a sulfate (SO_4^{2-}). However the resulting sulfates may be deposited on the carrier material, so that sulfates are adsorbed in the protective layer.

SO_2 molecules thus accumulate on the carrier and are stored there, while CO_2 molecules can penetrate through the protective layer without reacting. Theoretically, a single contact of an SO_2 molecule with the carrier surface provided with the oxidizing agent is sufficient to trigger the above-mentioned reaction, so complicated structures (such as those in a compressed powder pellet, for example) need not be formed in the protective layer to guarantee this one

contact with a probability bordering on certainty. Accordingly, CO_2 molecules need not penetrate through any complicated protective layer structure, so that CO_2 molecules can penetrate through the protective layer according to the present invention in a relatively unhindered and undelayed manner.

According to a preferred embodiment, the carrier may have at least one tube whose inside wall is provided with the oxidizing agent. In this embodiment, the SO_2 molecules and the CO_2 molecules penetrate through this tube axially, in which case there is a probability according to the laws of probability for the molecules striking the inside wall of the tube coated with the oxidizing agent. Due to this contact, an SO_2 molecule may become adsorbed on the carrier while a CO_2 molecule will rebound away from it without reacting and will continue on its way. The value for this adsorption probability can be determined as a function of a mean length of free path of the molecules by using a ratio of the cross section of the tube to the length of the tube.

Brief Description Of The Drawings

Figure 1 shows a longitudinal section through a first embodiment of the protective layer according to the present invention.

Figure 2 shows a perspective view of a second embodiment of the protective layer according to the present invention.

Figure 3 shows a side view of a third embodiment of the present invention.

Figure 4a shows a side view of a fourth embodiment of the protective layer according to the present invention.

Figure 4b shows a top view of a fourth embodiment according to the present invention.

Detailed Description

According to Figure 1, a smoke detector 3 is mounted on a wall 2 in a room 1, in particular on a room ceiling; in the event smoke develops in room 1, this smoke detector should deliver a warning signal accordingly. For this purpose, smoke detector 3 has a CO_2-sensitive sensor 4 equipped with a CO_2-sensitive membrane 5. In addition, smoke detector 3 has a carrier 10, which is designed here as a cylindrical tube 6, in particular a round cylindrical tube. In this embodiment, this tube 6 is part of a protective layer 7 according to the present invention which is marked by figure bracket 7. CO_2 sensor 4 here is separated from room 1 by this protective layer 7, i.e., by tube 6.

Tube 6 is mounted in an airtight mount on smoke detector 3 on one axial end, so that tube 6 encloses CO_2 sensor 4. The axial end of tube 6 opposite CO_2 sensor 4 is open and exposed to a gas present in room 1. An inside wall 8 of tube 6 is provided with a coating 9 of a nonvolatile oxidating agent. For example, potassium permanganate may be used as the oxidizing agent. Tube 6 may be made of aluminum oxide, for example.

The protective layer according to the present invention functions as follows:

As soon as an SO_2 molecule strikes inside wall 8 of tube 6 (the path of motion of such an SO_2 molecule is represented by an interrupted line), the SO_2 molecule is oxidized to an SO_3 molecule by the oxidizing agent, forming manganese dioxide (MnO_2). The acid anhydride SO_3 immediately reacts further to (SO_4^{2-}) and combines with released potassium compounds to form K_2SO_4. The solids formed by these reactions, namely MnO_2 and K_2SO_4, are deposited on inside wall 8 of tube 6, so that to this extent the SO_2 molecules are adsorbed by carrier 10 of layer 7 or by tube 6. Tube 6 is preferably made of a corrosion-resistant material that is resistant to sulfuric acid media, so that neither SO_2 nor SO_3 molecules nor (SO_4^{2-}) can damage tube 6.

In contrast with an SO_2 molecule, a CO_2 molecule (its path of motion represented by a solid line) is not adsorbed on inside wall 8 of tube 6, but instead is deflected, so that the CO_2 molecule can strike membrane 5 of CO_2 sensor 4 without any great delay. As soon as a sufficient quantity of CO_2 molecules striking membrane 5 has triggered the proper response, smoke alarm 3 delivers the warning signal.

According to Figure 2, carrier 10 of protective layer 7 according to the present invention may also be designed as a block which may be composed of a plurality of axially parallel cylindrical tubes 6 arranged side by side. In this embodiment, tubes 6 have a rectangular cross section, in particular a square cross section. Here again, inside walls 8 are provided with oxidizing agent coating 9.

Such block-like carriers 10 can be produced especially easily from monolithic catalysts, which then need only be provided with oxidizing agent coating 9.

According to Figure 3, carrier 10 of protective layer 7 may also be designed as a block, individual tubes 6 aligned radially with respect to a straight line perpendicular to the plane of the drawing or a point 11. In the specific embodiment illustrated in Figure 3, tubes 6 are not cylindrical in shape but instead they have a cross section tapering in the direction of the point or line 11. This embodiment allows molecules to penetrate into tubes 6 from a large solid angle range, so that CO_2 molecules can reach CO_2 sensor 4 from practically all directions.

According to Figures 4a and 4b, carrier 10 of protective layer 7 is again formed from a block, which here is composed of multiple grids 12 stacked one above the other, each being formed by a plurality of intersecting grid rods 13. Individual grids 12 need not be aligned with one another and stacked as in Figures 4a and 4b, and instead individual grids 12 may also be arranged with an offset. Oxide coating 9 here is applied to the surface of grid rods 13. The probability of adsorption is determined by the number of grids 12 stacked together and by their mesh; in other words, this is the probability that an SO_2 molecule penetrating into protective layer 7 will strike the surface of one of grid rods 13 and will react with the oxidizing agent there, thus being adsorbed in protective layer 7.

Abstract Of The Disclosure

A protective layer which is relatively permeable for CO_2 and relatively impermeable for SO_2 is designed so as to yield a reduced penetration time for CO_2 molecules. The protective layer is composed of a gas-permeable carrier made of a material which is resistant to sulfuric acid media such as SO_2 and SO_3, has a surface that can be exposed to a gas and is provided with an oxidizing agent whose oxidation potential is sufficient to oxidize SO_2.

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PROTECTIVE LAYER

Field Of The Invention [Background Information]

The present invention relates to a protective layer which is relatively permeable for CO_2 and is relatively impermeable for SO_2.

Background Information

Such a protective layer is used, for example, to protect a CO_2-sensitive polymer layer of a smoke detector from damage or contamination due to SO_2. Such a CO_2-sensitive polymer layer is used as a gas sensor in a smoke detector to detect a CO_2 content in a room where the smoke detector is installed. The CO_2-sensitive polymer layer preferably has a membrane composed of a polymer matrix (e.g., polydimethylsiloxane), an auxiliary base (tetraalkylammonium hydroxide) and a pH-sensitive dye (e.g., thymol blue or other derivatives). When this CO_2-sensitive membrane is exposed to CO_2, it leads to reversible reactions, preferably detectable by an optical [means] element, in particular also by electrical or mass-sensitive [means] elements, thus permitting an inference regarding the CO_2 content in the room monitored.

However, when this CO_2-sensitive membrane comes in contact with SO_2, it leads to irreversible reactions in the sensor material and thus to destruction of the CO_2-sensitive feature of the sensor. Since this reaction of the sensor membrane to SO_2 is irreversible, SO_2 reaction products accumulate on the membrane, so that even a low SO_2 concentration will damage the sensor membrane over a period of time and decreases its CO_2 sensitivity, so that a smoke detector equipped with such a CO_2-sensitive membrane sensor will ultimately become useless.

Known protective layers are designed as compressed powder pellets or granules which are

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relatively impermeable for SO_2 but relatively permeable for CO_2. Likewise, there are known molecular filters which utilize differences in the molecular structure of the CO_2 molecules and are thus relatively impermeable for SO_2 molecules and relatively permeable for CO_2 molecules. However, one disadvantage when such a protective layer is used to protect a CO_2 sensor is that the CO_2 molecules must first penetrate through this protective layer to reach the CO_2 sensor. Accordingly, the period of time needed for the CO_2 molecules to reach the CO_2 sensor may be greatly prolonged. This increase in time has an especially serious effect when the CO_2 molecules are in movement merely due to their temperature-related kinetic energy (Brownian motion) in the absence of a directional flow, which is usually the case in propagation of smoke in the event of a fire. When such a protective layer is then used in a smoke alarm, the response time of the smoke alarm is increased due to the period of time required for the gas molecules to penetrate through the protective layer; in other words, the period of time until the CO_2 sensor detects an elevated CO_2 concentration is longer.

[Advantages of the] Summary Of The Invention

The protective layer according to the present invention [having the features of Claim 1], however, has the advantage that the CO_2 molecules need only a relatively short period of time to penetrate through the protective layer. When using the protective layer according to the present invention in a smoke alarm, this yields the advantage that the lengthening of the response time of the smoke alarm due to the protective layer is reduced.

The present invention is based on the finding that the oxidation product of SO_2, namely SO_3, is a strongly oxidizing and hygroscopic acid anhydride which reacts further immediately to form a sulfate (SO_4^{2-}). However the resulting sulfates may be deposited on the carrier material, so that sulfates are adsorbed in the protective layer.

SO_2 molecules thus accumulate on the carrier and are stored there, while CO_2 molecules can penetrate through the protective layer without reacting. Theoretically, a single contact of an SO_2 molecule with the carrier surface provided with the oxidizing agent is sufficient to trigger the above-mentioned reaction, so complicated structures (such as those in a compressed powder pellet, for example) need not be formed in the protective layer to guarantee this one

contact with a probability bordering on certainty. Accordingly, CO_2 molecules need not penetrate through any complicated protective layer structure, so that CO_2 molecules can penetrate through the protective layer according to the present invention in a relatively unhindered and undelayed manner.

According to a preferred embodiment, the carrier may have at least one tube whose inside wall is provided with the oxidizing agent. In this embodiment, the SO_2 molecules and the CO_2 molecules [must] penetrate through this tube axially, in which case there is a probability according to the laws of probability for the molecules striking the inside wall of the tube coated with the oxidizing agent. Due to this contact, an SO_2 molecule may become adsorbed on the carrier while a CO_2 molecule will rebound away from it without reacting and will continue on its way. The value for this adsorption probability can be determined as a function of a mean length of free path of the molecules by using a ratio of the cross section of the tube to the length of the tube.

[Other important features and advantages of the protective layer according to the present invention are derived from the subordinate claims, the drawings and the respective description of the figures on the basis of the drawings.] Brief Description Of The Drawings

[Embodiments of the protective layer according to the present invention are shown in the drawings and are illustrated in greater detail below. The drawings show schematically:]

Figure 1 shows a longitudinal section through a first embodiment of the protective layer according to the present invention[,].

Figure 2 shows a perspective view of a second embodiment of the protective layer according to the present invention[,].

Figure 3 shows a side view of a third embodiment of the present invention[, and].

Figure [4] 4a shows a side view [(Figure 4a) and a top view (Figure 4b)] of a fourth embodiment of the protective layer according to the present invention.

Figure 4b shows a top view of a fourth embodiment according to the present invention.

Detailed Description [of Embodiments]

According to Figure 1, a smoke detector 3 is mounted on a wall 2 in a room 1, in particular on a room ceiling; in the event smoke develops in room 1, this smoke detector should deliver a warning signal accordingly. For this purpose, smoke detector 3 has a CO_2-sensitive sensor 4 equipped with a CO_2-sensitive membrane 5. In addition, smoke detector 3 has a carrier 10, which is designed here as a cylindrical tube 6, in particular a round cylindrical tube. In this embodiment, this tube 6 is part of a protective layer 7 according to the present invention which is marked by figure bracket 7. CO_2 sensor 4 here is separated from room 1 by this protective layer 7, i.e., by tube 6.

Tube 6 is mounted in an airtight mount on smoke detector 3 on one axial end, so that tube 6 encloses CO_2 sensor 4. The axial end of tube 6 opposite CO_2 sensor 4 is open and exposed to a gas present in room 1. An inside wall 8 of tube 6 is provided with a coating 9 of a nonvolatile oxidating agent. For example, potassium permanganate may be used as the oxidizing agent. Tube 6 may be made of aluminum oxide, for example.

The protective layer according to the present invention functions as follows:

As soon as an SO_2 molecule strikes inside wall 8 of tube 6 (the path of motion of such an SO_2 molecule is represented by an interrupted line), the SO_2 molecule is oxidized to an SO_3 molecule by the oxidizing agent, forming manganese dioxide (MnO_2). The acid anhydride SO_3 immediately reacts further to (SO_4^{2-}) and combines with released potassium compounds to form K_2SO_4. The solids formed by these reactions, namely MnO_2 and K_2SO_4, are deposited on inside wall 8 of tube 6, so that to this extent the SO_2 molecules are adsorbed by carrier 10 of layer 7 or by tube 6. Tube 6 is preferably made of a corrosion-resistant material that is resistant to sulfuric acid media, so that neither SO_2 nor SO_3 molecules nor (SO_4^{2-}) can damage tube 6.

In contrast with an SO_2 molecule, a CO_2 molecule (its path of motion represented by a solid

line) is not adsorbed on inside wall 8 of tube 6, but instead is deflected, so that the CO_2 molecule can strike membrane 5 of CO_2 sensor 4 without any great delay. As soon as a sufficient quantity of CO_2 molecules striking membrane 5 has triggered the proper response, smoke alarm 3 delivers the warning signal.

According to Figure 2, carrier 10 of protective layer 7 according to the present invention may also be designed as a block which may be composed of a plurality of axially parallel cylindrical tubes 6 arranged side by side. In this embodiment, tubes 6 have a rectangular cross section, in particular a square cross section. Here again, inside walls 8 are provided with oxidizing agent coating 9.

Such block-like carriers 10 can be produced especially easily from monolithic catalysts, which then need only be provided with oxidizing agent coating 9.

According to Figure 3, carrier 10 of protective layer 7 may also be designed as a block, individual tubes 6 aligned radially with respect to a straight line perpendicular to the plane of the drawing or a point 11. In the specific embodiment illustrated in Figure 3, tubes 6 are not cylindrical in shape but instead they have a cross section tapering in the direction of the point or line 11. This embodiment allows molecules to penetrate into tubes 6 from a large solid angle range, so that CO_2 molecules can reach CO_2 sensor 4 from practically all directions.

According to Figures 4a and 4b, carrier 10 of protective layer 7 is again formed from a block, which here is composed of multiple grids 12 stacked one above the other, each being formed by a plurality of intersecting grid rods 13. Individual grids 12 need not be aligned with one another and stacked as in Figures 4a and 4b, and instead individual grids 12 may also be arranged with an offset. Oxide coating 9 here is applied to the surface of grid rods 13. The probability of adsorption is determined by the number of grids 12 stacked together and by their mesh; in other words, this is the probability that an SO_2 molecule penetrating into protective layer 7 will strike the surface of one of grid rods 13 and will react with the oxidizing agent there, thus being adsorbed in protective layer 7.

Abstract Of The Disclosure

A protective layer [(7)] which is relatively permeable for CO_2 and relatively impermeable for SO_2 is designed so as to yield a reduced penetration time for CO_2 molecules. The protective layer [(7)] is composed of a gas-permeable carrier [(10)] made of a material which is resistant to sulfuric acid media such as SO_2 and SO_3, has a surface [(8)] that can be exposed to a gas and is provided with an oxidizing agent whose oxidation potential is sufficient to oxidize SO_2.

[(Figure 1)]

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PROTECTIVE LAYER

Background Information

The present invention relates to a protective layer which is relatively permeable for CO_2 and is relatively impermeable for SO_2. Such a protective layer is used, for example, to protect a CO_2-sensitive polymer layer of a smoke detector from damage or contamination due to SO_2. Such a CO_2-sensitive polymer layer is used as a gas sensor in a smoke detector to detect a CO_2 content in a room where the smoke detector is installed. The CO_2-sensitive polymer layer preferably has a membrane composed of a polymer matrix (e.g., polydimethylsiloxane), an auxiliary base (tetraalkylammonium hydroxide) and a pH-sensitive dye (e.g., thymol blue or other derivatives). When this CO_2-sensitive membrane is exposed to CO_2, it leads to reversible reactions, preferably detectable by optical means, in particular also by electrical or mass-sensitive means, thus permitting an inference regarding the CO_2 content in the room monitored.

However, when this CO_2-sensitive membrane comes in contact with SO_2, it leads to irreversible reactions in the sensor material and thus to destruction of the CO_2-sensitive feature of the sensor. Since this reaction of the sensor membrane to SO_2 is irreversible, SO_2 reaction products accumulate on the membrane, so that even a low SO_2 concentration will damage the sensor membrane over a period of time and decreases its CO_2 sensitivity, so that a smoke detector equipped with such a CO_2-sensitive membrane sensor will ultimately become useless.

Known protective layers are designed as compressed powder pellets or granules which are relatively impermeable for SO_2 but relatively permeable for CO_2. Likewise, there are known molecular filters which utilize differences in the molecular structure of the CO_2 molecules and are thus relatively impermeable for SO_2 molecules and relatively permeable for CO_2 molecules. However, one disadvantage when such a protective layer is used to protect a CO_2 sensor is that the CO_2 molecules must first penetrate through this protective layer to reach the

CO_2 sensor. Accordingly, the period of time needed for the CO_2 molecules to reach the CO_2 sensor may be greatly prolonged. This increase in time has an especially serious effect when the CO_2 molecules are in movement merely due to their temperature-related kinetic energy (Brownian motion) in the absence of a directional flow, which is usually the case in propagation of smoke in the event of a fire. When such a protective layer is then used in a smoke alarm, the response time of the smoke alarm is increased due to the period of time required for the gas molecules to penetrate through the protective layer; in other words, the period of time until the CO_2 sensor detects an elevated CO_2 concentration is longer.

Advantages of the Invention

The protective layer according to the present invention having the features of Claim 1, however, has the advantage that the CO_2 molecules need only a relatively short period of time to penetrate through the protective layer. When using the protective layer according to the present invention in a smoke alarm, this yields the advantage that the lengthening of the response time of the smoke alarm due to the protective layer is reduced.

The present invention is based on the finding that the oxidation product of SO_2, namely SO_3, is a strongly oxidizing and hygroscopic acid anhydride which reacts further immediately to form a sulfate (SO_4^{2-}). However the resulting sulfates may be deposited on the carrier material, so that sulfates are adsorbed in the protective layer.

SO_2 molecules thus accumulate on the carrier and are stored there, while CO_2 molecules can penetrate through the protective layer without reacting. Theoretically, a single contact of an SO_2 molecule with the carrier surface provided with the oxidizing agent is sufficient to trigger the above-mentioned reaction, so complicated structures (such as those in a compressed powder pellet, for example) need not be formed in the protective layer to guarantee this one contact with a probability bordering on certainty. Accordingly, CO_2 molecules need not penetrate through any complicated protective layer structure, so that CO_2 molecules can penetrate through the protective layer according to the present invention in a relatively unhindered and undelayed manner.

According to a preferred embodiment, the carrier may have at least one tube whose inside

wall is provided with the oxidizing agent. In this embodiment, the SO_2 molecules and the CO_2 molecules must penetrate through this tube axially, in which case there is a probability according to the laws of probability for the molecules striking the inside wall of the tube coated with the oxidizing agent. Due to this contact, an SO_2 molecule may become adsorbed on the carrier while a CO_2 molecule will rebound away from it without reacting and will continue on its way. The value for this adsorption probability can be determined as a function of a mean length of free path of the molecules by using a ratio of the cross section of the tube to the length of the tube.

Other important features and advantages of the protective layer according to the present invention are derived from the subordinate claims, the drawings and the respective description of the figures on the basis of the drawings.

Drawings

Embodiments of the protective layer according to the present invention are shown in the drawings and are illustrated in greater detail below. The drawings show schematically:

Figure 1 a longitudinal section through a first embodiment of the protective layer according to the present invention,

Figure 2 a perspective view of a second embodiment of the protective layer according to the present invention,

Figure 3 a side view of a third embodiment of the present invention, and

Figure 4 a side view (Figure 4a) and a top view (Figure 4b) of a fourth embodiment of the protective layer according to the present invention.

Description of Embodiments

According to Figure 1, a smoke detector 3 is mounted on a wall 2 in a room 1, in particular on a room ceiling; in the event smoke develops in room 1, this smoke detector should deliver

a warning signal accordingly. For this purpose, smoke detector 3 has a CO_2-sensitive sensor 4 equipped with a CO_2-sensitive membrane 5. In addition, smoke detector 3 has a carrier 10, which is designed here as a cylindrical tube 6, in particular a round cylindrical tube. In this embodiment, this tube 6 is part of a protective layer 7 according to the present invention which is marked by figure bracket 7. CO_2 sensor 4 here is separated from room 1 by this protective layer 7, i.e., by tube 6.

Tube 6 is mounted in an airtight mount on smoke detector 3 on one axial end, so that tube 6 encloses CO_2 sensor 4. The axial end of tube 6 opposite CO_2 sensor 4 is open and exposed to a gas present in room 1. An inside wall 8 of tube 6 is provided with a coating 9 of a nonvolatile oxidating agent. For example, potassium permanganate may be used as the oxidizing agent. Tube 6 may be made of aluminum oxide, for example.

The protective layer according to the present invention functions as follows:

As soon as an SO_2 molecule strikes inside wall 8 of tube 6 (the path of motion of such an SO_2 molecule is represented by an interrupted line), the SO_2 molecule is oxidized to an SO_3 molecule by the oxidizing agent, forming manganese dioxide (MnO_2). The acid anhydride SO_3 immediately reacts further to (SO_4^{2-}) and combines with released potassium compounds to form K_2SO_4. The solids formed by these reactions, namely MnO_2 and K_2SO_4, are deposited on inside wall 8 of tube 6, so that to this extent the SO_2 molecules are adsorbed by carrier 10 of layer 7 or by tube 6. Tube 6 is preferably made of a corrosion-resistant material that is resistant to sulfuric acid media, so that neither SO_2 nor SO_3 molecules nor (SO_4^{2-}) can damage tube 6.

In contrast with an SO_2 molecule, a CO_2 molecule (its path of motion represented by a solid line) is not adsorbed on inside wall 8 of tube 6, but instead is deflected, so that the CO_2 molecule can strike membrane 5 of CO_2 sensor 4 without any great delay. As soon as a sufficient quantity of CO_2 molecules striking membrane 5 has triggered the proper response, smoke alarm 3 delivers the warning signal.

According to Figure 2, carrier 10 of protective layer 7 according to the present invention may also be designed as a block which may be composed of a plurality of axially parallel

cylindrical tubes 6 arranged side by side. In this embodiment, tubes 6 have a rectangular cross section, in particular a square cross section. Here again, inside walls 8 are provided with oxidizing agent coating 9.

Such block-like carriers 10 can be produced especially easily from monolithic catalysts, which then need only be provided with oxidizing agent coating 9.

According to Figure 3, carrier 10 of protective layer 7 may also be designed as a block, individual tubes 6 aligned radially with respect to a straight line perpendicular to the plane of the drawing or a point 11. In the specific embodiment illustrated in Figure 3, tubes 6 are not cylindrical in shape but instead they have a cross section tapering in the direction of the point or line 11. This embodiment allows molecules to penetrate into tubes 6 from a large solid angle range, so that CO_2 molecules can reach CO_2 sensor 4 from practically all directions.

According to Figures 4a and 4b, carrier 10 of protective layer 7 is again formed from a block, which here is composed of multiple grids 12 stacked one above the other, each being formed by a plurality of intersecting grid rods 13. Individual grids 12 need not be aligned with one another and stacked as in Figures 4a and 4b, and instead individual grids 12 may also be arranged with an offset. Oxide coating 9 here is applied to the surface of grid rods 13. The probability of adsorption is determined by the number of grids 12 stacked together and by their mesh; in other words, this is the probability that an SO_2 molecule penetrating into protective layer 7 will strike the surface of one of grid rods 13 and will react with the oxidizing agent there, thus being adsorbed in protective layer 7.

What is claimed is:

1. A protective layer which is relatively permeable for CO_2 and is relatively impermeable for SO_2 and has a gas-permeable carrier (10) made of a material which is resistant to sulfuric acid media such as SO_2 and SO_3, and it has a surface (8) which can be exposed to a gas and is provided with an oxidizing agent whose oxidation potential is sufficient to oxidize SO_2.

2. The protective layer according to Claim 1, wherein a nonvolatile oxidizing agent is used.

3. The protective layer according to Claim 1 or 2, wherein potassium permanganate is used as the oxidizing agent.

4. The protective layer according to one of Claims 1 through 3, wherein the carrier (10) is made of aluminum oxide.

5. The protective layer according to one of Claims 1 through 4, wherein the carrier (10) has at least one tube (6) whose inside wall (8) is provided with the oxidizing agent.

6. The protective layer according to Claim 5, wherein the carrier (10) is designed as a block composed of a plurality of axially parallel cylindrical tubes (6) aligned side by side.

7. The protective layer according to Claim 5 or 6, wherein the tubes (6) are designed as round cylinders.

8. The protective layer according to Claim 5, wherein the carrier (10) is designed as a block composed of several tubes (6) arranged side by side in radial alignment relative to a straight line or a point (11).

9. The protective layer according to Claim 8, wherein the tubes (6) have a cross section which tapers toward the straight line or the point

(11).

10. The protective layer according to 1 of Claims 1 through 4, wherein the carrier (10) has at least one grid (12) composed of intersecting grid rods (13), the grid rods (13) being provided with oxidizing agent.

11. The protective layer according to Claim 10, wherein the carrier (10) is designed as a block composed of several grids (12) stacked one above the other.

12. A CO_2 sensor, in particular for a smoke detector, wherein the CO_2 sensor (4) is provided with a protective layer (7) according to one of the preceding claims, thus separating the CO_2 sensor (4) from a room (1) to be monitored for CO_2 content.

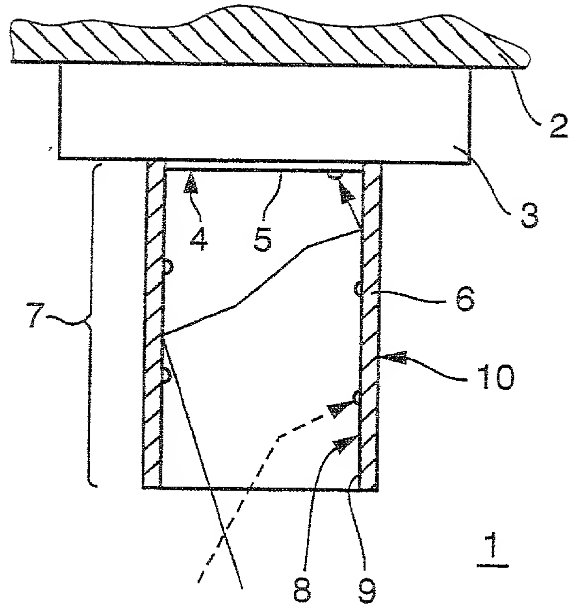

Fig. 1

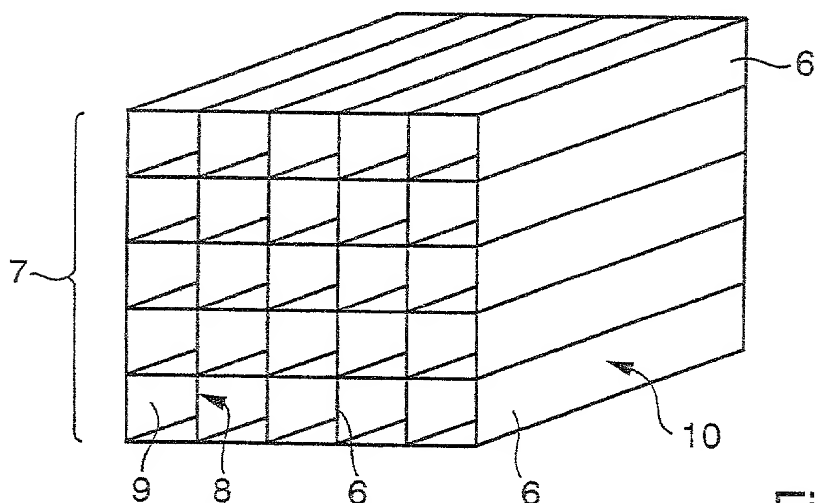

Fig. 2

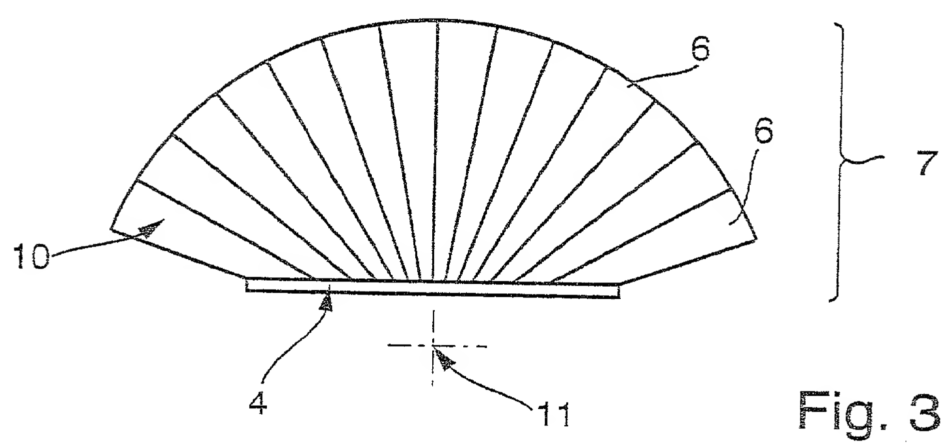

Fig. 3

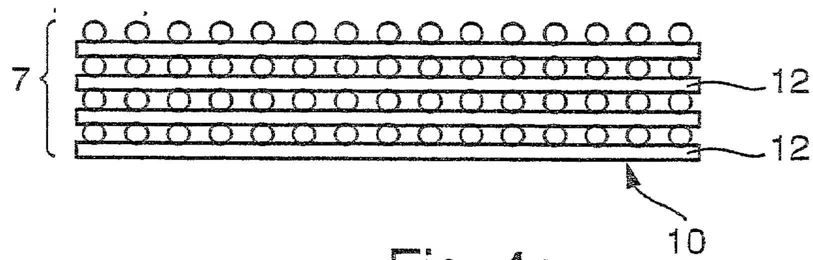

Fig. 4a

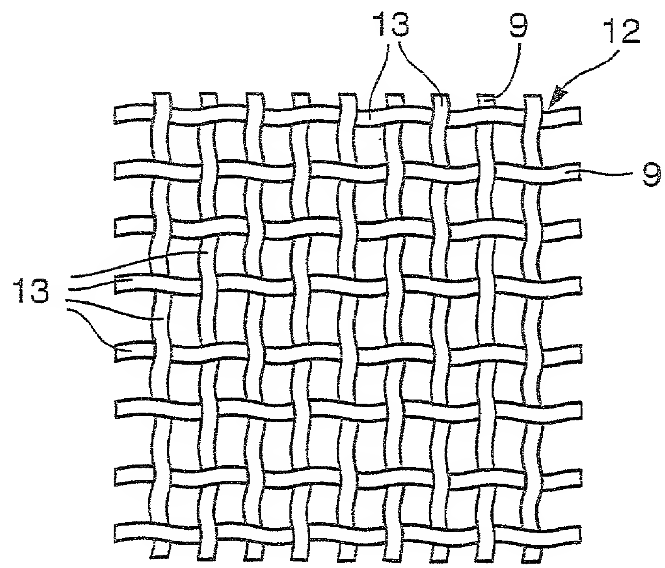

Fig. 4b

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[10191/1977]

COMBINED DECLARATION AND
POWER OF ATTORNEY FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below adjacent to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **PROTECTIVE LAYER**, and the specification of which:

[ ] is attached hereto;

[ ] was filed as United States Application Serial No.
and,

[X] was filed as PCT International Application Number PCT/DE00/00406, on the 11th day of February, 2000

[X] an English translation of which is filed herewith.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a). I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international applications(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

EV003627911

~~EL244504339~~

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119

Country : Federal Republic of Germany

Application No. : 199 05 776.1

Date of Filing: 12 February 1999

Priority Claimed
Under 35 U.S.C. § 119 : [x] Yes [ ] No

I hereby claim the benefit under Title 35, United States Code § 120 of any United States Application or PCT International Application designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations § 1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

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U.S. APPLICATIONS

Number :

Filing Date :

PCT APPLICATIONS
DESIGNATING THE U.S.

PCT Number :

PCT Filing Date :

I hereby appoint the following attorney(s) and/or agents to prosecute the above-identified application and transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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200

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